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Applicant(s) : Toyo Boseki Kabushiki Kaisha

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【Inventor】

【Address】 c/o Toyo Boseki Kabushiki Kaisha Research Center, 1-1, Katata 2-chome, Ohtsu-shi, Shiga, Japan

【Name】 Koji Syoki

【Inventor】

【Address】 c/o Toyo Boseki Kabushiki Kaisha Research Center, 1-1, Katata 2-chome, Ohtsu-shi, Shiga, Japan

【Name】 Keiichi Motoi

【Inventor】

【Address】 c/o Toyo Boseki Kabushiki Kaisha Research Center, 1-1, Katata 2-chome, Ohtsu-shi, Shiga, Japan

【Name】 Yuji Taguchi

【Applicant】

【Identification Number】 000003160

【Name】 Toyo Boseki Kabushiki Kaisha

【Representative】 Junji Tsumura

【Official Fee】

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【List of the Annexed Documents】

【Document】 Specification One copy

【Document】 Abstract One copy

【Proof】 Requested

【Document】 SPECIFICATION

【Title of the Invention】 PHOTOSENSITIVE RESIN LAMINATE AND PLATE FOR SIGNBOARD MADE THEREOF

【What is Claimed is】

【Claim 1】 A photosensitive resin laminate comprising at least a support, an adhesive layer and a photosensitive resin layer, wherein the photosensitive resin layer has an absorbance at 400 nm - 600 nm of not more than 0.3.

【Claim 2】 The photosensitive resin laminate of claim 1, wherein the photosensitive resin layer has a thickness of not less than 500 μm, and a Shore hardness of not less than 50.

【Claim 3】 The photosensitive resin laminate of claim 1 or claim 2, wherein the photosensitive resin layer has a scattering rate of not more than 25%.

【Claim 4】 The photosensitive resin laminate of any of claims 1 to 3, wherein the photosensitive resin layer has a turbidity of not more than 3.5.

【Claim 5】 The photosensitive resin laminate of any of claims 1 to 4, wherein the photosensitive resin layer contains a hydroxylamine derivative.

【Claim 6】 A plate for a signboard comprising the photosensitive resin laminate of any of claims 1 to 5.

【Detailed Description of the Invention】

【Technical Field to which the Invention Pertains】

The present invention relates to a photosensitive resin laminate and a plate for a signboard made thereof, which are used for signboards such as display panel, decoration shield, name plate, Braille board and the like. Particularly, the present invention provides a signboard superior in design.

【Prior Art】

A photosensitive resin layer exposed to light through a pattern and thereafter developed to produce a photosensitive resin laminate for signboard is disclosed in JP-A-58-55927, JP-A-9-6267 and the like and used for display panels having a

relief, signboards containing Braille and the like.

However, there is a demand in the market with regard to signboards in these days for bending processing during processing of signboards, producing transparent signboards and the like. However, a photosensitive resin laminate for general use, which comprises a phenol board as a support, is not suitable for bending during processing of a signboard or production of a transparent signboard. Even when a transparent and colorless substrate is used as a support, the photosensitive resin itself is colored. Accordingly, there has arisen a demand on a photosensitive resin laminate suitable for processing into a signboard having a good design.

A photosensitive resin composition contains a naphthoquinone compound and the like for the purpose of inhibiting thermal polymerization and for adjusting sensitivity and the like. Because of the color of these compounds themselves, production by a composition containing these compounds inevitably results in a colored photosensitive resin, which is problematic for use as a signboard having a superior design. Even if the amount of addition of these compounds is reduced with the hope of suppressing the coloring, the polymer becomes a gel during the production, thus practically preventing the production.

【Problems to be Solved by the Invention】

It is therefore an object of the present invention to obtain a photosensitive resin laminate for signboards usable for display panel, decoration shield, name plate, Braille board and the like, which laminate has a superior design, which can be bent during processing of a signboard, and from which a transparent signboard can be produced.

【Means of Solving the Problems】

The present inventors have conducted intensive studies in an attempt to solve the above-mentioned problems and completed the present invention. That is, the present invention provides

(1) A photosensitive resin laminate comprising at least a support, an adhesive layer and a photosensitive resin layer, wherein the photosensitive resin layer has an absorbance at 400 nm - 600 nm of not more than 0.3.

(2) The photosensitive resin laminate of the above-mentioned (1), wherein the photosensitive resin layer has a thickness of not less than 500 μm and a Shore hardness of not less than 50.

(3) The photosensitive resin laminate of the above-mentioned (1) or (2), wherein the photosensitive resin layer has a scattering rate of not more than 20%.

(4) The photosensitive resin laminate of any of the above-mentioned (1) to (3), wherein the photosensitive resin layer has a turbidity of not more than 3.5.

(5) The photosensitive resin laminate of any of the above-mentioned (1) to (4), wherein the photosensitive resin layer contains a hydroxylamine derivative.

(6) A plate for a signboard characterized by the use of the photosensitive resin laminate of any of the above-mentioned (1) to (5).

【Embodiment of the Invention】

The present invention is now explained in more detail.

The photosensitive resin layer in the present invention shows an absorbance at 400 nm - 600 nm of not more than 0.3, preferably not more than 0.2. When the absorbance exceeds 0.3, the photosensitive resin unpreferably becomes appreciably colored.

The photosensitive resin layer in the present invention preferably shows a scattering rate of not more than 25%, more preferably not more than 20%. When the scattering rate exceeds 25%, a slit depth which is among the printing properties, becomes unpreferably smaller.

The photosensitive resin layer in the present invention preferably shows a turbidity of not more than 3.5, particularly not more than 3.0. When the turbidity exceeds 3.5,

the photosensitive resin shows poor transparency, which is not preferable.

The photosensitive resin composition to be used in the present invention may be known, and is exemplified by a soluble polymer compound (e.g., poly(vinyl alcohol), polyamide, polyether ester amide, polyether amide, polyurethane and the like), photopolymerizable or photocrosslinkable monomer (e.g., acrylate of polyhydric alcohol, epoxy acrylate of polyhydric alcohol, N-methylolacrylamide and the like), photopolymerization initiator (e.g., benzyldimethyl ketal, benzoindimethyl ether and the like), and a photosensitive resin composition containing, where necessary, a plasticizer, a surfactant, a dye and the like.

While, in the present invention, one wherein each component of the aforementioned photosensitive resin composition is free from coloring is preferably selected, it is preferable to contain a hydroxylamine derivative in the present invention.

Examples of the hydroxylamine derivative include cupferron derivatives such as N-nitrosophenylhydroxylamine aluminum salt, N-nitrosophenylhydroxylamine ammonium salt and the like, cupferron analogs such as N-benzoylphenylhydroxylamine, benzohydroxamic acid, 3-hydroxyl-1,3-diphenyltriazine and the like, N,N-diethylhydroxylamine, and N-(t-butyl)hydroxylamine hydrochloride. Of these, N-nitrosophenylhydroxylamine aluminum salt and N-nitrosophenylhydroxylamine ammonium salt are particularly preferable in the present invention.

Referring to the mixing ratio of the aforementioned hydroxylamine derivatives, when the resin solid is less than 0.005 wt%, the thermal polymerization inhibitory effect is not exerted, causing polymer gelation at halfway during the production, whereas when it is not less than 0.05 wt%, the resin produced becomes colored, which is not preferable for

producing a transparent resin. Thus, to make the photosensitive resin layer transparent and colorless, the mixing ratio is preferably 0.005 - 0.05 wt%, particularly preferably 0.01 - 0.03 wt%.

Furthermore, hydroquinone, hydroquinone monomethyl ether, 2,6-di-t-butyl-p-cresol and the like may be added in a proportion of 0.001 - 5 wt% as a polymerization inhibitor. As a sensitivity adjusting agent, a compound having an absorption band at 300 - 400 nm may be added, such as naphthalene derivatives (e.g., phenothiazine, naphthoic acid and the like), anthracene derivatives (e.g., 9-hydroxyanthracene and the like), and the like. It is also possible to alter the properties of a photocured substance by adding a plasticizer, such as low molecular weight plasticizers (e.g., ester, amide and the like), and oligomers (e.g., polyester, polyether, liquid rubber and the like).

The aforementioned photosensitive resin layer preferably has a thickness of not less than 500 μm, particularly 800 - 1200 μm. The Shore hardness is preferably not less than 50, particularly preferably 55 - 65.

The support (hereinafter sometimes to be referred to as a supporting plate) to be used in the present invention has a thickness of preferably not less than 1 mm, and a thickness generally in the range of 1 mm - 10 mm is employed depending on the use and design. When the support has a thickness of less than 1 mm, the support itself may warp easily, which is not suitable for signboard use, whereas a thickness of not less than 10 mm is unpreferable because the plate does not cut easily and inconveniently weighs too much.

The material of the supporting plate may be a metal plate such as an aluminum plate, an iron plate and the like, a wood plate, a stone plate and the like, as well as a polymer formed plate of polyethylene terephthalate resin, acrylic resin and the like. Moreover, the polymer formed plate may be made from

a resin modified by copolymerization or blending or reformed by mixing with an additive such as a plasticizer and the like.

When the laminate of the present invention is used as a signboard, moreover, the design of the aforementioned supporting plate is reflected well. For example, when the supporting plate is an aluminum plate or a metal-plated resin plate, the signboard becomes metallic, and when it is a wooden board, the woodgrain is reflected on the signboard.

When the supporting plate is also transparent and a design is printed on the supporting plate side, a signboard having the design is produced.

For production of the photosensitive resin laminate of the present invention, an adhesive to be mentioned later is applied on the aforementioned supporting plate and a photosensitive resin layer is laminated, which can be performed by a known method. For example, an optional method, such as heat press, injection molding, melt extrusion, solution casting, lamination and the like, can be employed to perform lamination on the aforementioned support.

The aforementioned photosensitive resin layer may be laminated in advance on, for example, a resin film of polyethylene terephthalate and the like as a support (hereinafter to be referred to as a photosensitive resin laminate precursor) and, when preparing a signboard therefrom, it is laminated on the aforementioned supporting plate having a thickness of not less than 1 mm upon peeling off of the resin film.

The aforementioned photosensitive resin laminate precursor can be prepared by a method generally employed for forming a photosensitive resin laminate for a printing plate. For example, a photosensitive resin composition is melt-extruded in between the aforementioned resin film (preferably without an adhesive in this case) and a 125 μm-thick polyester cover film having a layer of non-adhesive transparent polymer

that can be dispersed or dissolved in a developing solution [(poly(vinyl alcohol), celluloses and the like, which is also called a slip coat layer)] in a thickness of 1 - 3 μm, whereby a photosensitive resin laminate precursor comprising a resin film, a photosensitive resin layer, a slip coat layer and a cover film in this order from the bottom can be obtained.

In the present invention, the adhesive layer used for adhering a photosensitive resin layer (optionally having a slip coat layer and a cover film) to the aforementioned supporting plate may be a known adhesive. Examples thereof include polyester urethane adhesives wherein a soluble polyester is cured with polyhydric isocyanate, epoxy adhesives and the like. Of these, polyester urethane adhesive is preferable because it is superior in the adhesion to polyethylene terephthalate resin and modified polyethylene terephthalate resin. The adhesive layer composition may contain small amounts of other components. Examples of the additive include plasticizer, dye, ultraviolet absorber, halation preventive, surfactant, photopolymerizable vinyl monomer and the like.

An adhesive layer is formed on a supporting plate typically by applying a solution of the composition for adhesive layer in a predetermined thickness and removing the solvent. The application method may be known, such as roll coater, curtain flow coater, slit die coater, gravure coater, spray and the like. The adhesive layer after coating on a supporting plate is generally dried by blowing hot air in a drying furnace. The adhesive layer of the present invention may be dried at not less than 30°C and not more than 120°C for a suitable period of time, but a temprerature of not more than 70 °C is preferable in view of thermal deformation of the supporting plate. The treatment for 1 min - 30 min is appropriate.

The adhesive layer preferably has a thickness of 0.5 μ -

100 μ. When the thickness is not more than 0.5 μ, the adhesive power is difficult to achieve between the photosensitive resin layer and the adhesive layer, whereas when it exceeds 100 μ, a problem of entrained bubbles occurs due to foaming during drying of the liquid applied. In view of the above, the adhesive layer preferably has a thickness of 0.5 μ - 100 μ, particularly preferably 1 μ - 50 μ.

A signboard can be prepared from the photosensitive resin laminate of the present invention comprising a supporting plate, an adhesive layer and a photosensitive resin layer, which may further have a slip coat layer and a cover film, according to a method generally used for producing printing plates. For example, a negative film or positive film having a transparent image part is closely adhered onto a photosensitive resin layer via a slip coat layer or otherwise, and an actinic ray is shot thereon to insolubilize and cure only the exposed part. The actinic radiation is obtained from a light source generally having a wavelength of 300 - 450 nm, such as high pressure mercury lamp, ultrahigh pressure mercury lamp, metal halide lamp, xenon lamp, chemical lamp and the like.

Then, an unexposed part is removed by dissolution in a suitable solvent, particularly neutral water in the present invention, whereby a relief having a clear image part is obtained. For this end, spray developing apparatus, brush developing apparatus and the like can be used.

Following the above methods, a signboard having a relief can be produced. Various signboards can be obtained, which expands the range of use, by applying a paint containing colorant, ultraviolet absorber and the like to the relief, putting gold leaf on letters and images, applying a paint, adding a pigment to a support, drawing a pattern on the back of the support or coloring the support, adhering a decorative laminate sheet and the like, or where necessary, bending while

heating the support and the like.

[Examples]

The present invention is explained in detail by referring to examples. The present invention is not limited by these examples in any way. The evaluations in Examples are the values measured according to the following methods.

1) Measurement of absorbance at 400 - 600 nm

Photosensitive resin compositions 1-4 were cut out in 30 mm × 70 mm, and the absorbance at 400 - 600 nm was measured with a self-recording spectrophotometer (U-3210, Hitachi, Ltd.).

2) Measurement of scattering rate of transmitted light

Photosensitive resin compositions 1-4 were cut out in 30 mm × 70 mm and heated at 95°C for 3 min, which was subjected to the measurement of scattering rate at 360 nm using a self-recording spectrophotometer (U-3210, Hitachi, Ltd.).

3) Measurement of turbidity

Turbidity was measured using a turbidimeter (haze meter, NDH-1001DP Nippon Denshoku Industries Co., Ltd.).

Example 1

As the photosensitive resin composition to be laminated, ε-caprolactam (525 parts), nylon salt (400 parts) of N-(2-aminoethyl)piperazine and adipic acid, and nylon salt (75 parts) of 1,3-bis(aminomethyl)cyclohexane and adipic acid were subjected to melt condensation polymerization in an autoclave to give a nylon copolymer. The obtained polymer (55 parts), N-nitrosophenylhydroxylamine aluminum salt (0.01 part), hydroquinone monoethyl ether (0.1 part) and N-ethyltoluenesulfonamide (7 parts) were dissolved in a mixed solvent of methanol (47 parts) and water (96 parts) at 60°C, and glycidyl methacrylate (2 parts) was added. The mixture was stirred for 2 h to allow reaction of glycidyl methacrylate with the polymer terminal. To this solution were added ammonium sulfite (0.3 part), oxalic acid (0.3 part) and

methacrylic acid (4 parts), after which acrylate (31 parts) obtained by opening addition reaction of triglycidyl ether of trimethylolpropane and acrylic acid, and benzyl dimethyl ketal (1.0 part) were added to give a solution of a photosensitive resin composition. This solution was cast on a polyester film and methanol was evaporated to give a photosensitive resin composition 1 having a thickness of about 800 μm.

A modified polyethylene terephthalate resin having a Shore D hardness of 60°, a thickness of 1.5 mm and a total light transmission of 80%, which is a polyethylene terephthalate resin obtained by copolymerizing isophthalic acid (10 mol%), was used as a support.

As an adhesive layer, used was a polyester urethane adhesive, and a solution of the composition for adhesive layer was prepared as follows. A polyester resin (VYLON RV-200, 80 parts by weight, Toyo Boseki Kabushiki Kaisha) was heated and dissolved in a mixed solvent (1940 parts by weight) of toluene/methyl ethyl ketone=80/20 (weight ratio) at 80°C. After cooling, DESMODUER HL (20 parts by weight, Sumitomo Bayer Urethane) obtained from hexamethylene diisocyanate and toluene diisocyanate was used as an isocyanurate type polyhydric isocyanate, and triethylenediamine (0.06 part by weight) was added as a curing catalyst, after which the mixture was stirred for 10 min.

The thus-obtained solution of the composition for adhesive layer was applied on a polyethylene terephthalate plate having a thickness of 1.5 mm, such that a film thickness was 7 μm, cure-dried at 50°C for 15 min to give a support having an adhesive layer.

The photosensitive resin laminate composition obtained as above and the support which had an adhesive layer were adhered and water was poured therebetween. A photosensitive resin layer was press-adhered at room temperature at 25°C by passing the laminate through a rubber roller whose gap

clearance had been adjusted according to the thickness of the laminate, to give a transparent and colorless photosensitive resin laminate 1.

Example 2

Phenothiazine (0.04 part) was added instead of N-nitrosophenylhydroxylamine aluminum salt (0.01 part) in Example 1, a photosensitive resin composition 2 was produced.

In the same manner as in Example 1, a photosensitive resin laminate 2 was produced.

Example 3

In the same manner as in Example 1, a copolymerized nylon polymer (55 parts), N-nitrosophenylhydroxylamine aluminum salt (0.01 part), hydroquinone monoethyl ether (0.1 part) and N-ethyltoluenesulfonamide (7 parts) were dissolved in a mixed solvent of methanol (47 parts) and water (96 parts) at 60°C, and glycidyl methacrylate (2 parts) was added. The mixture was stirred for 2 h to allow reaction of glycidyl methacrylate with the polymer terminal. To this solution were added ammonium sulfite (0.3 part), oxalic acid (0.3 part) and methacrylic acid (4 parts), after which acrylate (31 parts) obtained by opening addition reaction of triglycidyl ether of trimethylolpropane and acrylic acid, benzyl dimethyl ketal (1.0 part) and phenothiazine (0.02 part) were added to give a solution of a photosensitive resin composition. This solution was cast on a polyester film and methanol was evaporated to give a photosensitive resin composition 3 having a thickness of about 800 μm.

In the same manner as in Example 1, a photosensitive resin laminate 3 was produced.

Comparative Example 1

1,4-Naphthoquinone (0.04 part) was added instead of N-nitrosophenylhydroxylamine aluminum salt (0.01 part) in Example 1, a photosensitive resin composition 4 was produced.

In the same manner as in Example 1, a photosensitive

resin laminate 4 was produced.

Reference Example 1

The above-mentioned photosensitive resin laminates 1-4 were preserved for not less than 7 days, and a polyester film of 125 μm was peeled off, and the test negative films (gray scale negative film for sensitivity measurement and image negative film for image reproducibility evaluation) were adhered in vacuo and exposed to light from a chemical lamp for 3 min. Using a brush washer (100 μmϕ nylon brush, NIHON DENSHI SEIKI CO. LTD., JW-A2-PD type) and tap water as a developing solution, the negatives were developed at 23°C for 2 min to give a relief image. The photosensitive resin laminates were dried with warm air at 60°C for 5 min and exposed to light from an ultrahigh pressure mercury lamp for 30 sec, after which the obtained relief was evaluated. The results are shown in Table 1.

Table 1

		Example 1	Example 2	Example 3	Comp. Example 1
		Photosensitive resin laminate 1	Photosensitive resin laminate 2	Photosensitive resin laminate 3	Photosensitive resin laminate 4
composition	appearance of image	transparent and colorless	transparent and colorless	transparent and colorless	brown and transparent
	absorbance at 400-600 nm	<0.2	<0.2	<0.2	0.4-0.8
	scattering rate	12%	13%	15%	23%
	turbidity	3.1	2.3	2.9	4.4
relief properties	gray scale	12 step	12 step	12 step	12 step
	reproducibility of isolated dot	200 μm	200 μm	200 μm	200 μm
	reproducibility of fine line	40 μm	40 μm	40 μm	40 μm
	600 μm slit depth	138 μm	143 μm	145 μm	144 μm

【Effect of the Invention】

The above-mentioned photosensitive resin laminate of the present invention has a transparent photosensitive resin layer. This has an effect that the design of the support can be reflected well, and a signboard having any design can be produced depending on the material of the support, printed pattern and the like. In addition, the support can be bent easily, which enables provision of a photosensitive resin laminate suitable for a signboard, thus greatly contributing to the industry.

【Document】 Abstract

【Summary】

【Problems】 Provision of a photosensitive resin laminate, which is used for signboards such as display panel, decoration shield, name plate, Braille board and the like, and particularly superior in design.

【Solving Means】 (1) A photosensitive resin laminate comprising at least a support, an adhesive layer and a photosensitive resin layer, wherein the photosensitive resin layer has an absorbance at 400 nm - 600 nm of not more than 0.3. (2) The photosensitive resin laminate of the above-mentioned (1), wherein the photosensitive resin layer has a thickness of not less than 500 μm and a Shore hardness of not less than 50. (3) The photosensitive resin laminate of the above-mentioned (1) or (2), wherein the photosensitive resin layer has a scattering rate of not more than 20%. (4) The photosensitive resin laminate of any of the above-mentioned (1) to (3), wherein the photosensitive resin layer has a turbidity of not more than 3.5. (5) The photosensitive resin laminate of any of the above-mentioned (1) to (4), wherein the photosensitive resin layer contains a hydroxylamine derivative. (6) A plate for a signboard characterized by the use of the photosensitive resin laminate of any of the above-mentioned (1) to (5).

【Main Drawing】 None